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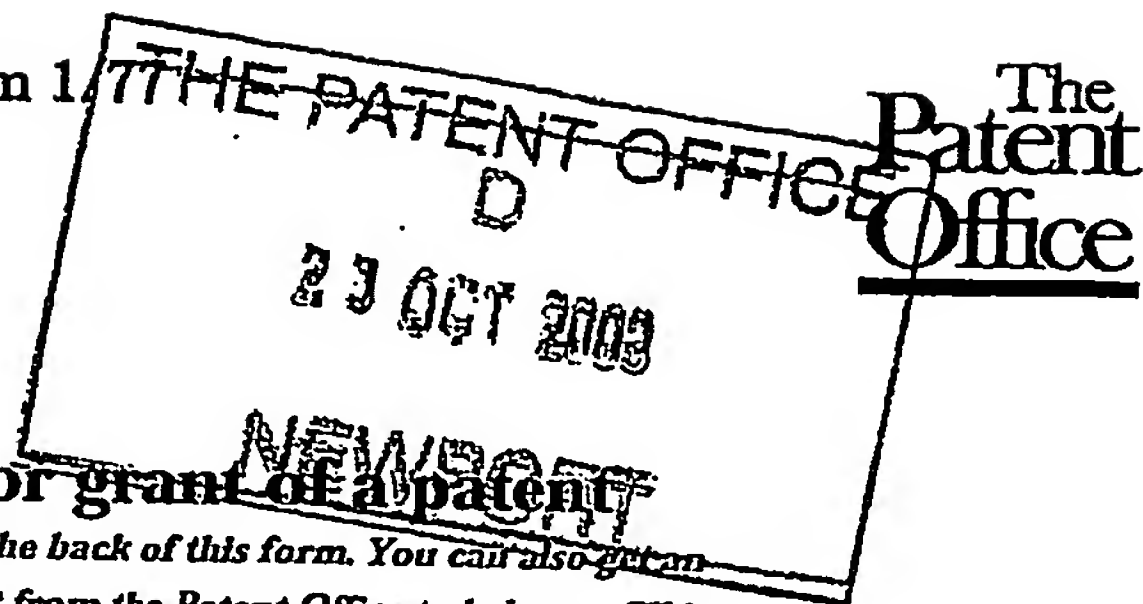
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*Andrew Giersey*

Dated 20 September 2004



23 OCT 03 E846594.1 002914  
F01/7700.01.00-0324673.3

## Request for grant of a patent

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The Patent Office

Cardiff Road  
Newport  
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NP9 1RH

1. Your reference

SN140

2. Patent application number

(The Patent Office will fill in this part)

0324673.3

23 OCT 2003

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)

DOW CORNING CORPORATION

DOW CORNING ASIA LTD

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Patents ADP number (*if you know it*)

8506060002

Tokyo 100-0005

If the applicant is a corporate body, give the country/state of its incorporation

USA/Michigan

7882376001  
Japan

4. Title of the invention

PROCESS FOR CONTROLLING FOAM

5. Name of your agent (*if you have one*)

P V DAVIES

"Address for service" in the United Kingdom  
to which all correspondence should be sent  
(*including the postcode*)

DOW CORNING LIMITED  
Intellectual Property Department  
Cardiff Road  
Barry  
CF63 2YL

Patents ADP number (*if you know it*)

4140307001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*if you know it*) the or each application number

Country

Priority application number  
(*if you know it*)Date of filing  
(*day / month / year*)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(*day / month / year*)8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (*Answer 'Yes' if*

Yes

- a) any applicant named in part 3 is not an inventor, or  
b) there is an inventor who is not named as an applicant, or  
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Continuation sheets of this form

Description 9

Claim(s) 3

Abstract

Drawing(s) 2 *2*

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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

1 fee sheet

11. I/We request the grant of a patent on the basis of this application.

Signature *P V Davies*  
P V Davies

Date 22/10/2003

12. Name and daytime telephone number of person to contact in the United Kingdom  
P V Davies 01446 723 505

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PROCESS FOR CONTROLLING FOAM

## FIELD OF THE INVENTION

5 [0001] This invention relates to a process for controlling foaming and to a foam control agent. In particular it relates to controlling foaming during an aqueous alcoholic fermentation process.

## BACKGROUND TO THE INVENTION

10

[0002] Fermentation processes have long been known for the production of beverages and more recently are being used for the preparation of alcohol for fuel from molasses, corn syrup or sugar cane juice. During the course of the fermentation, the microorganisms release carbon dioxide bubbles, which produce foam. The proteins which are in the fermentation  
15 broth stabilise the air/water interphase and thus stabilise the foam.

[0003] The main technology currently used in the fuel alcohol fermentation industry is based on the use of a "foam conditioner" made of a polyglycol, for example an ethylene oxide (EO) – propylene oxide (PO) copolymer and of mineral oil-based antifoam. This solution  
20 requires the use of two materials and the low persistency of these antifoam agents means that new antifoam material has to be added on a regular basis.

[0004] Silicones have been widely used as foam control agents in various industries. There have been suggestions to use silicones as foam control agents in fermentation  
25 processes. FR-A-2508471 describes a foam control agent comprising a polydimethylsiloxane of viscosity at least  $20 \times 10^{-6} \text{ m}^2/\text{sec.}$ , silica, polyoxypropylene, a nonionic surface active agent and a dispersion agent. US-A-6083998 describes a defoamer comprising polydimethylsiloxane, an ethylene oxide propylene oxide block copolymer and a silicone / silica blend.

## SUMMARY OF THE INVENTION

[0005] We have found according to the invention that certain silicones not usually employed as foam control agents are particularly effective in controlling foam in fermentation processes, particularly in the preparation of alcohol for fuel.

[0006] According to one aspect of the invention a process for controlling foaming during an aqueous alcoholic fermentation process comprises adding a hydroxy-functional polydiorganosiloxane of viscosity 10 to 150 mPa.s to the aqueous fermenting liquor.

[0007] The hydroxy-functional polydiorganosiloxanes of viscosity 10 to 150 mPa.s are miscible with many polyglycols, and we have found that such mixtures are also particularly effective in controlling foam in the preparation of alcohol for fuel. Thus according to another aspect of the invention a foam control agent for an aqueous alcoholic fermentation process comprises a blend of a hydroxy-functional polydiorganosiloxane of viscosity 10 to 150 mPa.s and a polyglycol with which the hydroxy-functional polydiorganosiloxane is miscible.

## DETAILED DESCRIPTION OF THE INVENTION

[0008] The hydroxy-functional polydiorganosiloxane is preferably a silanol-functional polydiorganosiloxane, particularly a silanol-terminated polydiorganosiloxane such as a silanol-terminated polydimethylsiloxane (PDMS). Siloxanes containing other organic groups linked to silicon such as 2-4C alkyl or phenyl can be used. The silanol-terminated PDMS preferably has a viscosity of at least 20 cSt (equivalent to about 20 mPa.s) up to about 50 cSt. 'Dow Corning PA Fluid' (Trade Mark), having a viscosity of about 42 cSt, is one example of a suitable fluid.

[0009] The hydroxy-functional polydiorganosiloxane can alternatively be a polydiorganosiloxane containing silicon-bonded hydroxyalkyl groups having 1 to 4 carbon atoms, for example methylol groups. Such hydroxyalkyl groups are preferably at the terminal



position of the polydiorganosiloxane, but can alternatively be substituted elsewhere than at the terminal position.

5 [0010] The hydroxy-functional polydiorganosiloxane is preferably added at 5 to 250 parts per million by volume based on the aqueous fermenting liquor, for example at 10 to 200  $\mu$ l per litre of fermenting liquor.

10 [0011] The hydroxy-functional polydiorganosiloxane can be added to the aqueous fermenting liquor unmixed with any additive. In one process according to the invention, a silanol-terminated polydiorganosiloxane is the only foam control added to the aqueous fermenting liquor.

[0012] Alternatively, a polyglycol with which the hydroxy-functional polydiorganosiloxane is miscible can also be added to the aqueous fermenting liquor. By  
15 "miscible" we mean that the polyglycol and the hydroxy-functional polydiorganosiloxane are miscible in the proportions used without requiring any emulsifier or cosolvent. The polyglycol is a hydroxy-terminated polyether. The polyglycol can for example be of molecular weight 400 up to 4000. Many silanol-terminated polydiorganosiloxanes are miscible with hydroxy-terminated polyoxypropylene, hydroxy-terminated polytetramethylene  
20 oxide and hydroxy-terminated oxyethylene-oxypropylene copolymers. In general miscibility increases with decreasing viscosity of the polydiorganosiloxane and with decreasing molecular weight of the polyether. For example, silanol-terminated PDMS of viscosity up to about 50 mPa.s is miscible with polyoxypropylene of molecular weight 2000, but PDMS of viscosity 50 to 150 mPa.s is miscible with polypropylene glycol of lower molecular weight.  
25 The polyglycol can be added separately from the hydroxy-functional polydiorganosiloxane but is preferably added admixed with the hydroxy-functional polydiorganosiloxane, for example in a weight ratio of hydroxy-functional polydiorganosiloxane to polyglycol in the range 5:1 to 1:5.

30 [0013] The hydroxy-functional polydiorganosiloxane, or the mixture of polyglycol and hydroxy-functional polydiorganosiloxane, can be mixed with up to 50% by weight based on the hydroxy-functional polydiorganosiloxane of a branched silicone resin. The branched

silicone resin is generally a non-linear siloxane resin and preferably consists of siloxane units of the formula  $R'_aSiO_{4-a/2}$  wherein  $R'$  denotes a hydroxyl, hydrocarbon or hydrocarbonoxy group, and wherein  $a$  has an average value of from 0.5 to 2.4. It preferably consists of monovalent trihydrocarbonsiloxy (M) groups of the formula  $R''_3SiO_{1/2}$  and tetrafunctional (Q) groups  $SiO_{4/2}$  wherein  $R''$  denotes a monovalent hydrocarbon group. The number ratio of M groups to Q groups is preferably in the range 0.4:1 to 2.5:1, most preferably 0.5:1 to 0.8:1. The silicone resin can for example be present at 1 to 40%, preferably 5 to 30%, based on the hydroxy-functional polydiorganosiloxane. Such a silicone resin can enhance the foam control efficiency of the hydroxy-functional polydiorganosiloxane.

[0014] The hydroxy-functional polydiorganosiloxane, or the mixture of polyglycol and hydroxy-functional polydiorganosiloxane, can be mixed with up to 150% by weight based on the hydroxy-functional polydiorganosiloxane of a silicone polyether. The silicone polyether can for example be a silicone polyether block copolymer or a comb-type copolymer having polyether chains pendant to a silicone backbone. Examples of a suitable silicone polyether is sold under the Trade Mark 'Dow Corning FS 1270' and 'Dow Corning FS83'. The silicone polyether is not required to compatibilise the hydroxy-functional polydiorganosiloxane and polyglycol but may enhance the foam control efficiency of the hydroxy-functional polydiorganosiloxane. The silicone polyether can for example be present at 1 to 100%, preferably 10 to 80%, based on the hydroxy-functional polydiorganosiloxane.

[0015] The hydroxy-functional polydiorganosiloxane, or the mixture of polyglycol and hydroxy-functional polydiorganosiloxane, can be mixed with up to 75% by weight based on the hydroxy-functional polydiorganosiloxane of a trialkylsilyl-terminated polydiorganosiloxane, for example a trimethylsilyl-terminated PDMS, although such a trialkylsilyl-terminated polydiorganosiloxane generally does not enhance the foam control efficiency of the hydroxy-functional polydiorganosiloxane. If used, the trialkylsilyl-terminated polydiorganosiloxane preferably has a viscosity in the range 5 to 250 mPa.s.

[0016] Conventional foam control agents generally contain hydrophobic fillers which are particulate materials solid at 100°C such as silica. We have found that such fillers may enhance, but are not critical for the foam control efficiency of the hydroxy-functional

polydiorganosiloxane in aqueous fermenting liquors. The hydroxy-functional polydiorganosiloxane added as foam control agent according to the invention preferably contains no solid particles.

5 [0017] The hydroxy-functional polydiorganosiloxane, and the polyglycol and any other additive to the silanol-terminated polydiorganosiloxane, can be added continuously or intermittently to the aqueous fermenting liquor. Intermittent addition of 5 to 250  $\mu$ l foam control agent per litre of fermenting liquor every 10 to 60 minutes may be found most convenient.

10

[0018] In an alternative process, the hydroxy-functional polydiorganosiloxane, and the polyglycol and any other additive to the hydroxy-functional polydiorganosiloxane, are added initially to the aqueous fermenting liquor and an organic oil composition based on a hydrocarbon oil or vegetable oil is subsequently added to control foaming. Industrial scale  
15 fermentation tanks of 100,000 litres or more take a few hours to fill, and foam formation during filling of the tank is a particular problem. We have found that an initial charge of hydroxy-functional polydiorganosiloxane composition followed by subsequent additions of an organic oil based antifoam combine to give very efficient control of foaming. The organic oil can for example be a mineral oil such as a hydrogenated mineral oil or white oil, liquid  
20 polyisobutene, or an isoparaffinic oil, or can be a vegetable oil such as peanut oil, coconut oil, cottonseed oil or linseed oil. The organic oil can be mixed with a hydrophobic filler such as treated silica or ethylenebisstearamide, and/or a polyglycol.

[0019] The invention is illustrated by the following Examples, in which parts and  
25 percentages are by weight unless otherwise stated. The Examples will be described with reference to the accompanying drawings, of which

Figure 1 is a graph showing foam volume over time using the foam control agent of Example 1 or 2 according to the invention, or commercial foam control products currently used in the  
30 fuel alcohol fermentation industry, in the experimental test described in Example 1;



Figure 2 is a graph showing foam volume over time when the foam control agent of Example 3 or 4 is used as initial foam control agent with subsequent addition of an organic oil antifoam compared to the use of a commercial foam control product currently used in the fuel alcohol fermentation industry in the experimental test of Example 3;

Figure 3 is a graph showing foam volume over time when the foam control agent of Example 5 or 6 is used as initial foam control agent with subsequent addition of an organic oil antifoam compared to the use of a commercial foam control product currently used in the fuel alcohol fermentation industry in the experimental test of Example 3.

#### Examples 1 and 2

[0020] In Example 1, 'Dow Corning PA Fluid' silanol-terminated polydiorganosiloxane was used as foam control agent.

[0021] In Example 2, 50% 'Dow Corning PA Fluid' was mixed with 50% polypropylene glycol of molecular weight about 2000 to form a foam control agent.

[0022] A sparge test method was used to assess the antifoam efficiency of the foam control agents of Examples 1 and 2 compared to commercial products currently used in the fuel alcohol fermentation industry. The sparge test is made of a simple 1-liter graduated cylinder at the bottom of which an air diffuser is placed.

[0023] 85.7 g molasses of 70% non-volatile content (NVC) were dispersed in 214.3 g of Orval (Trade Mark) beer to obtain 300 g of diluted molasses of 20 °BRIX concentration: 45 g of yeast was dispersed in 55 g of Orval beer and pH was adjusted to 2.0 by addition of HCl aliquots. Beer is used to better reproduce the fermentation broth, as alcohol is produced as soon as the fermentation starts. 300 g of the molasses dispersion was blended with 100 g of the yeast dispersion to form an aqueous fermenting liquor. 400 ml of the aqueous fermenting liquor was poured into the cylinder. The antifoam (initially 20 µl) was added at the extremity of a Teflon rod, which is then introduced in the cylinder. The aqueous fermenting liquor was agitated to ensure good dispersion of the foam conditioner.

The air diffuser was then placed at the bottom of the cylinder to start the experiment. Foam levels were recorded as a function of time. Once the foam level reached the top of the cylinder, additional antifoam was added to control the foam.

5 [0024] Figure 1 shows that 20 microliter of 'Dow Corning PA Fluid' is required to control the foam during 20 minutes

[0025] Figure 1 also shows that addition of 20 microliters of the blend of 50% 'Dow Corning PA Fluid' and 50% polypropylene glycol as foam control agent enables the foam to  
10 be controlled during 35 minutes, demonstrating even better antifoam efficiency.

[0026] In the comparative experiment, 20 microliter of 'Pluronic PE 6100' (Trade Mark) hydroxy-terminated oxyethylene-oxypropylene copolymer was used initially as the foam conditioner and subsequent additions of 10 microliter of 'ARATROP 505' (Trade  
15 Mark) mineral oil based antifoam commercial product, these being the proportions in which these materials are added in commercial practice. Figure 1 shows that in order to control the foam during 20 minutes, the required antifoam content is 20 microliter of Pluronic PE 6100 and 40 microliters of ARATROP oil-based antifoam, for a total of 60  $\mu$ l of foam control agent. The amount of 'Dow Corning PA fluid' required to control the foam during 20  
20 minutes is thus three times less than the reference material.

#### Examples 3 and 4

[0027] The foam control agents of Examples 1 and 2 were each used as a "foam  
25 conditioner", that is to say they were added to a fermenting liquor as the initial foam control followed by addition of an organic oil antifoam.

[0028] The foam control agents were tested in a sparge test column of which bottom is made of glass frit. Air is blown through the frit to generate air bubbles during the  
30 experiment. Solid yeast was dispersed in water to reach a 40% solid content and pH was adjusted to 2.0 by addition of HCl aliquots. Sugar cane molasses was diluted till a 24 Brix solution is obtained. 300 ml of the yeast dispersion was blended with 600 ml of the sugar

syrup in a beaker. 40µl of the foam control agent ("foam conditioner") were added and gently dispersed with a spatula. All the liquid is poured in the column. Air flow was then started, with a flow rate of 10 l/min. When the foam level reached a given limit (set arbitrarily at 30 cm cylinder height), 'Aratrop 606' (Trade Mark) organic oil antifoam comprising mineral oil and ethylenebisstearamide was added (20 µl at a time). Foam collapse was followed by further foam increase, leading if necessary to further organic oil antifoam addition. The test was finished after 10 minutes. The results are shown in Figure 2.

[0029] In the above test of Example 3, where PA fluid is used initially as "foam conditioner", 40µl of the organic oil antifoam were needed over 10 minutes (required foam control agent: 40µl PA fluid + 40µl ARATROP 606)

[0030] In the test of Example 4, where a mixture of 50% 'Dow Corning PA Fluid' and 50% polypropylene glycol was used as foam conditioner, addition of 40 microliters of organic oil antifoam enables the foam to be controlled during 10 minutes (required foam control agent: 40 µl PA fluid/P2000 + 40 µl ARATROP 606).

[0031] By comparison, when the polyglycol blend DISP 9100 (Trade Mark) was used alone as initial foam conditioner, 200 µl of the organic oil antifoam were needed over 10 minutes (required foam control agent: 40 µl DISP 9100 + 200 µl ARATROP 606).

#### Example 5

[0032] 40% 'Dow Corning PA Fluid' was mixed with 40% of the polypropylene glycol of molecular weight about 2000 and 20% 'Dow Corning FS 1270' silicone polyether to form a foam control agent.

Example 6

[0033] 45% 'Dow Corning PA Fluid' was mixed with 45% of the polypropylene glycol of molecular weight about 2000 and 10% 'Dow Corning DC 9138' branched silicone resin to form a foam control agent

[0034] The foam control agents of Examples 5 and 6 were each tested in the sparge test described in Example 3 but using a sugar cane coming from a different origin.

10 [0035] In Example 5, only 20  $\mu$ l of the organic oil antifoam was needed over 10 minutes (required foam control agent: 40  $\mu$ l foam conditioner from example 5 + 20  $\mu$ l ARATROP 606).

15 [0036] In Example 6 also, only one addition of 20  $\mu$ l of the organic oil antifoam was needed (required foam control agent: 40  $\mu$ l foam conditioner from example 6 + 20  $\mu$ l ARATROP 606).

20 [0037] The results of the tests of Examples 5 and 6 are shown in Figure 3 compared to the use of DISP 9100 (Trade Mark) blend of polyglycols is added originally as foam conditioner. Four additions of organic oil antifoam were needed to control the foam for 10 minutes when DISP 9100 was added originally as foam conditioner (required foam control agent: 40  $\mu$ l DISP 9100 + 80  $\mu$ l ARATROP 606).

CLAIMS

1. A process for controlling foaming during an aqueous alcoholic fermentation process, comprising adding a hydroxy-functional polydiorganosiloxane of viscosity 10 to 150 mPa.s to the aqueous fermenting liquor.
2. A process according to Claim 1, characterised in that the hydroxy-functional polydiorganosiloxane is added at 5 to 250 parts per million by volume based on the aqueous fermenting liquor.
3. A process according to Claim 1 or Claim 2, characterised in that the hydroxy-functional polydiorganosiloxane is a silanol-terminated polydiorganosiloxane.
4. A process according to Claim 3, characterised in that the silanol-terminated polydiorganosiloxane is added to the aqueous fermenting liquor unmixed with any additive.
5. A process according to Claim 1 or Claim 2, characterised in that the hydroxy-functional polydiorganosiloxane contains silicon-bonded hydroxyalkyl groups having 1 to 4 carbon atoms.
6. A process according to any of Claims 1 to 3 or 5, characterised in that a polyglycol with which the hydroxy-functional polydiorganosiloxane is miscible is also added to the aqueous fermenting liquor.
7. A process according to Claim 6, characterised in that the hydroxy-functional polydiorganosiloxane is mixed with up to 200% by weight of the said polyglycol.
8. A process according to any of Claims 1 to 3 or 5, characterised in that the hydroxy-functional polydiorganosiloxane is mixed with up to 50% by weight



based on the hydroxy-functional polydiorganosiloxane of a branched silicone resin

9. A process according to any of Claims 1 to 3 or 5, characterised in that the hydroxy-functional polydiorganosiloxane is mixed with up to 150% by weight based on the hydroxy-functional polydiorganosiloxane of a silicone polyether
10. A process according to any of Claims 1 to 3 or 5, characterised in that the hydroxy-functional polydiorganosiloxane is mixed with up to 75% by weight based on the hydroxy-functional polydiorganosiloxane of a trialkylsilyl-terminated polydiorganosiloxane.
11. A process according to any of Claims 1 to 10, characterised in that the hydroxy-functional polydiorganosiloxane contains no solid particles.
12. A process according to any of Claims 1 to 11, characterised in that the hydroxy-functional polydiorganosiloxane is added initially to the aqueous fermenting liquor and an organic oil composition based on a hydrocarbon oil or vegetable oil is subsequently added to control foaming.
13. A foam control agent for an aqueous alcoholic fermentation process, comprising a blend of a hydroxy-functional polydiorganosiloxane of viscosity 10 to 150 mPa.s and a polyglycol with which the hydroxy-functional polydiorganosiloxane is miscible.
14. A foam control agent according to Claim 13, characterised in that the weight ratio of hydroxy-functional polydiorganosiloxane to polyglycol is in the range 5:1 to 1:2.
15. A foam control agent according to Claim 13 or Claim 14, characterised in that the polyglycol is a hydroxy-terminated polyoxypropylene or oxyethylene-oxypropylene copolymer.

16. A foam control agent according to any of Claims 13 to 15 which further contains up to 50% by weight based on the hydroxy-functional polydiorganosiloxane of a branched silicone resin
17. A foam control agent according to any of Claims 13 to 16 which further contains up to 150% by weight based on the hydroxy-functional polydiorganosiloxane of a silicone polyether.
18. Use of a hydroxy-functional polydiorganosiloxane of viscosity 10 to 150 mPa.s in controlling foaming during an aqueous alcoholic fermentation process.

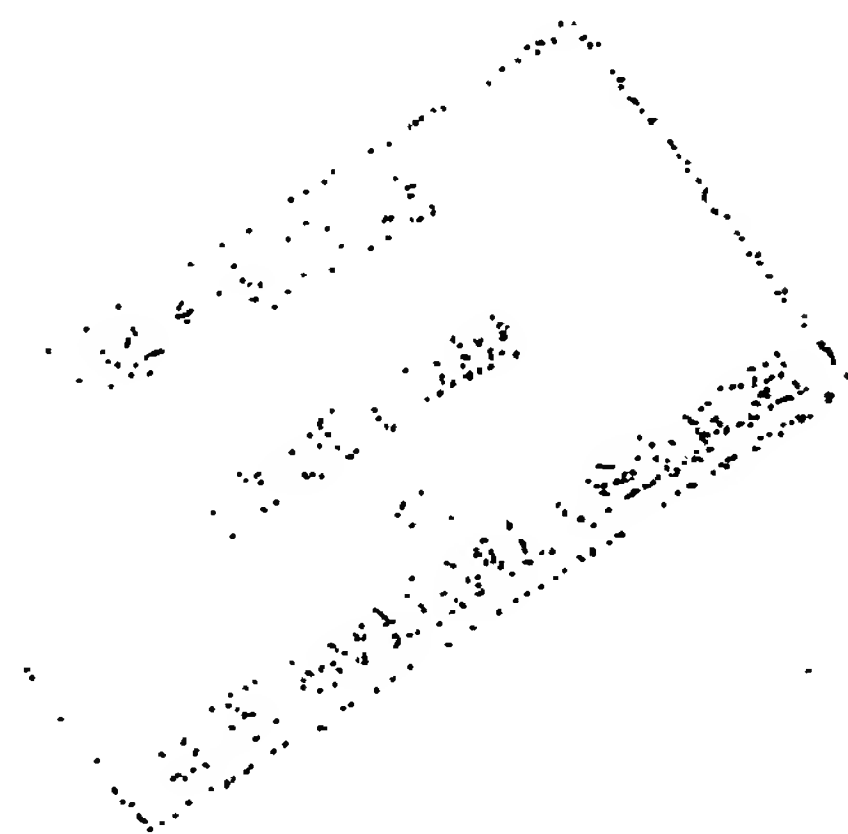


Figure 1

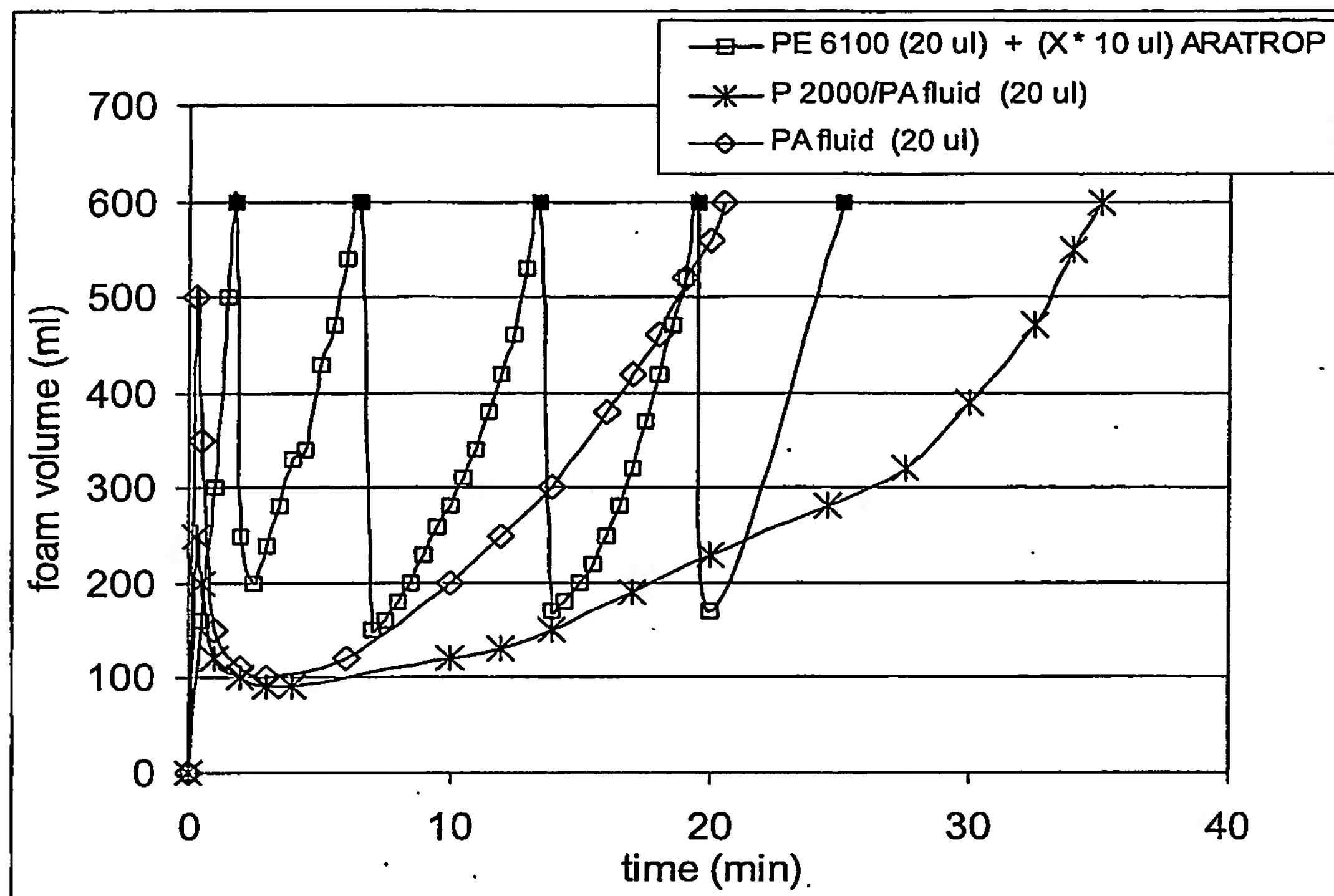


Figure 2

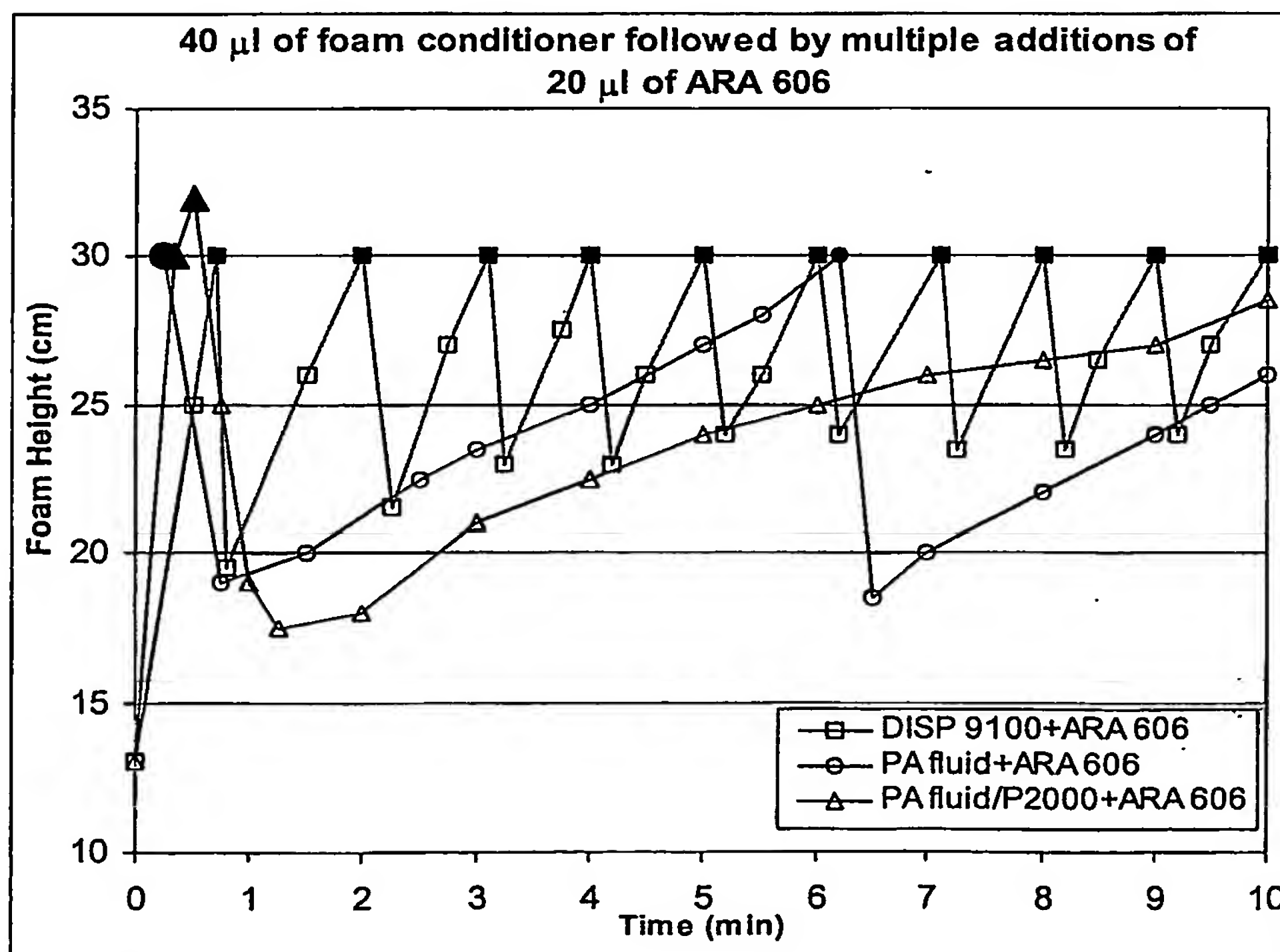


Figure 3

